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High energy density additives for Hybrid Fuel Rockets to Improve Performance and Enhance Safety

[Center Innovation Fund: ARC CIF Program](#)

- Public Data

Project Introduction

Abstract

We propose a conceptual study of prototype strained hydrocarbon molecules as high energy density additives for hybrid rocket fuels to boost the performance of these rockets without compromising safety and reliability. Use of these additives could extend the range of applications for which hybrid rockets become an attractive alternative to conventional solid or liquid fuel rockets.

The objectives of the study were to confirm and quantify the high enthalpy of these strained molecules and to assess improvement in rocket performance that would be expected if these additives were blended with conventional fuels. We confirmed the chemical properties (including enthalpy) of these additives. However, the predicted improvement in rocket performance was too small to make this a useful strategy for boosting hybrid rocket performance.

Detailed Description

Hybrid rockets use a solid fuel with a liquid or gaseous oxidizer. They have advantages over solid fuel rockets for certain space applications because the solid fuel component is more stable than a combined solid fuel and oxidizer, and have advantages over liquid fuel rockets because the fuel does not require cryogenic storage or pumping and the burn rate can be controlled by regulating the flow of oxidizer. Ideal fuels should exhibit a fast regression rate, high density and good mechanical stability (so it will not break apart during burning). A current project at ARC is to evaluate hybrid rockets comprised of solid paraffin fuel and cryogenic nitrous oxide and LOX oxidizer and has shown that higher regression rates are needed. Strained cyclic hydrocarbons have positive enthalpy and can be blended with paraffins to make fuels for hybrid rockets, but to be effective the resulting solid must have physical and mechanical characteristics at least comparable to the pure paraffin fuels. The stable hydrocarbon molecules with the highest strain energy are comprised of triangular rings of carbon atoms (cyclopropane), but these are gases at normal temperatures and pressures. Recently, chemists have synthesized molecules (called ivyanes, shown in Figure 1) containing multiple cyclopropane rings bonded together. We propose investigating blends of ivyanes and paraffins to determine their

thermochemical and physical properties. We will first carry out simulations to predict the enthalpy, density and stability of these blends using first principles chemistry and physics methods. Previously, first principles calculations by two of us (Jaffe and Zehe, J. Organic Chem. 2010, 75, 4387) demonstrated thermochemical properties can be determined to an accuracy of 2 kJ/mol for hydrocarbon molecules containing 10-20 carbon atoms. In the second phase, the density, melting temperature and heat of sublimation of solid ivyanes and the blends will be determined from molecular dynamics simulations.

Project Library (conference paper)

AIAA2013-3968 Characterization and Evaluation of High Energy Hydrocarbon Additives for Paraffin-Fuel Hybrid Rockets

Technologies Within this Project

This technology is categorized as a hardware component or part for other applications

Technology Details: High energy density additives for Hybrid Fuel Rockets to Improve Performance and Enhance Safety

Hybrid rockets use a solid fuel with a liquid or gaseous oxidizer. They have advantages over solid fuel rockets for certain space applications because the solid fuel component is more stable than a combined solid fuel and oxidizer, and have advantages over liquid fuel rockets because the fuel does not require cryogenic storage or pumping and the burn rate can be controlled by regulating the flow of oxidizer. Ideal fuels should exhibit a fast regression rate, high density and good mechanical stability (so it will not break apart during burning). A current project at ARC is to evaluate hybrid rockets comprised of solid paraffin fuel and cryogenic nitrous oxide and LOX oxidizer and has shown that higher regression rates are needed. Strained cyclic hydrocarbons have positive enthalpy and can be blended with paraffins to make fuels for hybrid rockets, but to be effective the resulting solid must have physical and mechanical characteristics at least comparable to the pure paraffin fuels. The stable hydrocarbon molecules with the highest strain energy are comprised of triangular rings of carbon atoms (cyclopropane), but these are gases at normal temperatures and pressures. Recently, chemists have synthesized molecules (called ivyanes, shown in Figure 1) containing multiple cyclopropane rings bonded together. We propose investigating blends of ivyanes and paraffins to determine their thermochemical and physical properties. We will first carry out simulations to predict the enthalpy, density and stability of these blends using first principles chemistry and physics methods. Previously, first principles calculations by two of us (Jaffe and Zehe, J. Organic

Chem. 2010, 75, 4387) demonstrated thermochemical properties can be determined to an accuracy of 2 kJ/mol for hydrocarbon molecules containing 10-20 carbon atoms. In the second phase, the density, melting temperature and heat of sublimation of solid ivyanes and the blends will be determined from molecular dynamics simulations.

Capabilities provided:

Use of hydrocarbon additives could solve problems of fuel pellet break up encountered with aluminum or lithium additives without sacrificing higher regression rates (burn rates), and lead to enhanced safety and lower cost compared to solid and liquid rocket propulsion systems.

Potential applications:

Mars sample return, in-space propulsion, upper-stage launch vehicle

Anticipated Benefits

Benefits to NASA funded missions

Any NASA funded mission that is using hybrid fuel rocket technology can benefit from this technology.

U.S. Locations Working on this Project

NASA Organizations Performing Work	Role	Location
<ul style="list-style-type: none">Ames Research Center (ARC)	Lead Center	Moffett Field, CA
<ul style="list-style-type: none">Ames Research Center (ARC)	Supporting Center	Moffett Field, CA
<ul style="list-style-type: none">Glenn Research Center (GRC)	Supporting Center	Cleveland, OH

U.S. States with Work:

U.S. States and Territories with Work on this Project

California

Share or Follow this Project

Organizational Responsibility

Responsible Mission Directorate:

Space Technology Mission Directorate (STMD)

Lead Center:

Ames Research Center (ARC)

Responsible Program:

Center Innovation Fund: ARC CIF Program

Project Management

Program Executive:

- Mino Dastoor

Program Manager:

- John Hines

Project Manager:

- Richard Jaffe

Principal Investigator:

- Richard Jaffe

Project Technology Areas

Primary:

- Launch Propulsion Systems (TA01)
 - Unconventional / Other Propulsion Systems (TA01.5)

Secondary:

- In-Space Propulsion Technologies (TA02)

Project Duration

Start Date: Aug 2011

End Date: Jan 2012

Project Technology Maturity

- At Start: 1
- Current: 1
- At End: 3

- 1
- 2
- 3
- 4
- 5
- 6
- 7
- 8
- 9

- Applied Research
- Development
- Demo & Test

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Characterization and Evaluation of High Energy Hydrocarbon Additives for Paraffin-Fuel Hybrid Rockets

Richard L. Jaffe,¹ Arif Karabeyoglu,² Brian Evans,³
 Gregory G. Zilliac,⁴ and Michael S. Sherburn⁵

Highly strained hydrocarbons called ivyanes are evaluated as a potential additive to boost the burn rate and I_{sp} for liquefying paraffin hybrid rockets. Ivyanes, which consist of cyclopropane rings bonded together, were first prepared in 2011 and have promise as a High Energy Density Material (HEDM) for propulsion and combustion applications. Differential Scanning Calorimetry (DSC) measurements were carried out on samples of ivyane and an ivyane-paraffin blend to measure phase changes and thermal stability. Quantum chemistry calculations were carried out using the G3MP2//B3LYP method to predict heats of formation and combustion for gas phase ivyanes. For validation purposes, calculations were also carried out for normal alkanes. Chemical equilibrium analysis was used to estimate the performance of ivyanes relative to paraffin for typical rocket engine scenarios. In addition, thermochemical properties of some plausible chemically modified ivyanes were modeled determine if they would improve rocket engine performance.

1. Introduction.

Hybrid rockets utilizing solid fuel and liquid or gaseous oxidizers have certain advantages over solid and liquid rockets, for example the fuel is stable and the oxidizer can be throttled to control the burn rate and even stop and restart the engine. Recent work at NASA Ames Research Center has focused on developing a liquefying paraffin fuel for hybrid rockets. To this end, tests have been carried out using a prototype engine named Peregrine^{1,2}. Although the performance of this engine is promising, on-going work is directed at enhancing the burn rate and specific impulse (I_{sp}). One avenue of research is to evaluate the potential of using a highly energetic molecular additive as a fuel component.

For more than 40 years the rocket design community has been searching for a way to boost the performance of rocket engines. In the Soviet Union scientists came up with a liquid hydrocarbon fuel called syntin^{3,4} that they started using in the second stage engine of the Soyuz-U2 rocket. It has the chemical proper chemical name 1-methyl-1,2-dicyclopropylcyclopropane, $C_{10}H_{16}$, and is comprised of three cyclopropyl rings joined

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together (Fig. 1). It has a positive enthalpy of formation (+199.2 kJ/mol (gas) and +151.9 kJ/mol (liq.)) and an estimated strain energy (from the cyclopropyl rings) of 313.6 kJ/mol. After the demise of the Soviet Union production of syntin was stopped because it was too expensive to produce for the amount of performance improvement as a rocket fuel.

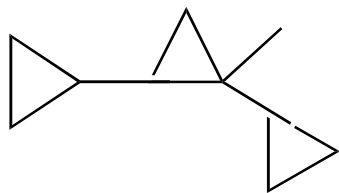


Figure 1. Schematic drawing of syntin. Each triangle represents a cyclopropyl ring with each vertex representing one carbon atom. The lines represent C-C bonds. Hydrogen atoms are not shown. The end of the dangling line from the middle triangle represents a methyl group (CH_3).

In the United States, NASA and the Air Force had their own programs to develop energetic rocket fuels or fuel additives. The Air Force Office of Scientific Research (AFOSR) program begun in 1987 was called HEDM⁵ (High Energy Density Materials) and was at its peak in the mid 1990s. It supported exploratory research to identify candidate fuel components. That program studied strained hydrocarbons like cubane^{6,7} (C_8H_8), which has one carbon at each vertex of a cube, and clusters of nitrogen atoms⁸ such as tetrahedral N_4 , N_3^+ and N_5^- . Cubane has very high strain energy because the angles between adjacent C-C bonds are compressed to 90° from the optimal value of 109.5° in tetrahedral carbon. The strain energy of molecules like cubane translates into a higher heat of combustion when the fuel is burned. Similarly, when heated to their decomposition temperature, nitrogen clusters are converted to diatomic nitrogen, releasing considerable heat. Much of the research supported by HEDM was based on modeling and simulation. In practice it proved very difficult and expensive to actually synthesize the proposed molecules and the program was terminated.

One recently synthesized family of hydrocarbons based on cyclopropyl rings is called ivyanes⁹. Cyclopropane (C_3H_6), has an equilateral triangle geometry with 60° angles between adjacent C-C bonds and one of the largest strain energies of all known hydrocarbons. Ivyanes (shown in Figure 2) have multiple cyclopropyl rings and are ideal HEDM candidates. They are especially attractive as additives for liquid kerosene and solid paraffin fueled rockets, because they have similar chemical compositions to these fuels, which should mean that these components would form stable blends. An added benefit is that the ivyane synthesis is simple compared to most other HEDM candidates, thereby reducing the cost of manufacture.

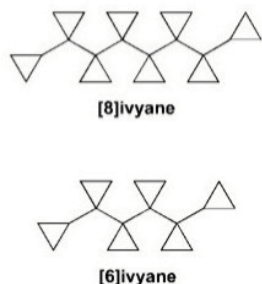


Figure 2. Schematic drawings of two ivyanes. Each vertex of a triangle represents one carbon atom and the lines represent C-C bonds. Two hydrogen atoms (not shown) are bonded to each carbon atom except for the backbone atoms (i.e., where the triangular rings are linked together).

In the present study, we are interested in potential additives for the Peregrine rocket engine, and are therefore interested in additives for solid paraffin. To be effective, a potential additive should have the following properties: (1) high positive formation enthalpy ($\Delta_f H^\circ$), (2) melting temperature similar to that of paraffin, (3) stoichiometry such that the ratio of hydrogen to carbon atoms (H/C) is as high as possible in order to maximize I_{sp} , (4) complete miscibility with paraffin, and (5) low cost. The specific impulse is a measure of rocket engine efficiency¹⁰ and has units of seconds. It is the ratio of the thrust generated by exhaust gases to the product of the gravitational constant and the mass flow rate in the exhaust. Having a faster fuel burn rate and lower average molecular weight for the exhaust gases increases I_{sp} . When hydrocarbon fuels are burned, all the carbon atoms are converted into CO_2 (44 g/mol) and all the hydrogen atoms are converted into H_2O (18 g/mol). Thus, a higher H/C ratio in the fuel results in a lower average molecular weight and higher exit velocity of the exhaust gases.

The paraffin used for the Peregrine project is a mixture of unbranched alkane chains with an average chain length of 32 ($C_{32}H_{66}$), a melt temperature of 69 C and $\Delta_f H^\circ(s) = -933$ kJ/mol¹¹. Ivyanes have been prepared as chains with up to eight cyclopropane rings and are sketched in Figure 2 (n in the notation $[n]$ ivyane, refers to the number of cyclopropane rings). [7]- and [8]ivyane ($C_{21}H_{30}$ and $C_{24}H_{34}$, respectively) are solids and ivyanes with lower $[n]$ are liquids at room temperature. The heat of combustion has been determined for [6]ivyane(l): $\Delta_c H^\circ = -12,300 \pm 600$ kJ/mol⁹ or -50.8 kJ/g, which is equivalent to $\Delta_f H^\circ = +1500 \pm 600$ kJ/mol. In comparison, paraffin has a heat of combustion of -21,092 kJ/mol or 46.9 kJ/g. According to these data, [6]ivyane releases ~8% more energy per gram than paraffin when burned. On the other hand, the H/C ratio is 2.06 for paraffin compared to 1.41-1.44 for ivyanes. For overall performance, higher energy release favors ivyanes, but the H/C ratio favors paraffin. I_{sp} is dependent on both.

The present paper describes the characterization of ivyanes and an assessment their suitability for use in paraffin-fuel hybrid rockets. For this project we obtained small samples of [6]- and [7]ivyane from the Sherburn research group at the Australian National University, Canberra, Australia, where it was first synthesized. In the next section we describe the physical properties of ivyanes, including data obtained from analysis of the samples we received⁹. In Section 3 we discuss computational studies of ivyanes to confirm and predict their heats of combustion and formation. In addition we discuss variations of the ivyane chemical structure that might lead to improved performance as a rocket fuel additive. In Section 4 we present an assessment of the performance of ivyane and the proposed variations in an idealized rocket engine using a thermochemical equilibrium model and comment on the prospects for this family of strained hydrocarbons as a rocket fuel or fuel additive.

2. Physical Characteristics of Ivyanes

Sherburn and coworkers, first reported the synthesis of a class of 1,1-oligocyclopropanes, called ivyanes, in 2011⁹. These molecules have numerous cyclopropyl groups bonded together like a string of pearls. The 60° angle between adjacent carbon-carbon bonds in cyclopropyl imparts high strain energy to the ring, as the optimal (i.e., strain free) angle between carbon-carbon bonds is 109.5°. Ivyane chains with up to 8 cyclopropyl rings have been prepared. Chains with up to 6 cyclopropyl groups are liquid at room temperature and those with 7 or more are waxy solids. In Sherburn's nomenclature [n]ivyane refers to a molecule with n cyclopropyl groups (empirical formula $C_{3n}H_{4n+2}$). The ivyanes were prepared in one step from another class of molecules called [n]dendralenes¹² shown in Figure 3. Each [n]dendralene has n carbon-carbon double bonds that can be converted into cyclopropyl rings. Dendralenes are easy to synthesize with up to 6 double bonds, but longer ones have been prepared as well. Sherburn reported some of the physical properties of the [n]ivyanes in the supplemental material that accompanied the original publication⁹. Included are bomb calorimetry measurements of the heat of combustion of [6]ivyane that show it to have a standard enthalpy of combustion, $\Delta_c H^\circ$, equal to $-12,300 \pm 600$ kJ/mol, which is equivalent to -50.8 kJ/g. This result makes [6]ivyane one of the most highly strained hydrocarbons known.

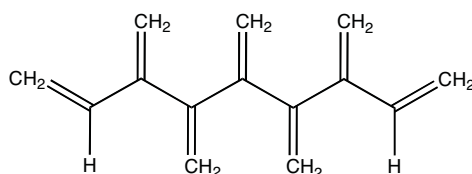


Figure 3. Schematic drawing of [7]dendralene. The double lines represent the carbon-carbon double bonds. The details of the figure are similar to those in Figures 1 and 2 except that all hydrogen atoms are shown.

The goals of the experimental characterization are to determine the melt and boiling temperatures, density, heats of fusion and vaporization and thermal stability of the pure samples. To assess their miscibility with paraffin, a small sample of a 1:1 paraffin-[7]ivyane blend (by weight) has been prepared by melting the solid mixture followed by cooling to room temperature.

Differential scanning calorimetry (DSC)¹³ was carried out for samples of the pure components and the blend. DSC measures the heat flow into and out of a sample as the temperature is raised and then lowered at a controlled rate (in this case ± 2 C/minute). In the absence of phase changes or chemical reactions, the amount of heat needed to raise the temperature of the sample is small and proportional to the heat capacity. When the sample melts or vaporizes additional heat is required to overcome the enthalpy of fusion or vaporization. This is an endothermic change in the sample and shows up as a dip in the heat flow. When the sample undergoes oxidation or thermal decomposition heat is released and the heat flow curve has a peak. DSC measurements require only ~10 mg

samples. Figures 4 and 5 show the DSC results for [7]ivyane and the 1:1P-I blend. The deep feature at ~ 50 C in both figures is the melt transition that occurs as the samples are heated. In Figure 4a and 5 an open sample container was used and the sample reacted with atmospheric oxygen when the temperature was increased above 250 C. In Figure 4b and 4c the sample was in a closed container and the high temperature peaks (Figure 4c) are indicative of non-oxidative decomposition. No boiling transition was observed. The fact that the melt transitions for [7]ivyane and the 1:1 P-I blend are similar suggests that the components are well mixed in the blend. However the melt transition occurs over a broader temperature range in the blend, because the melt temperature of [7]ivyane is around 20 C lower than pure paraffin (shown in Figure 6). The phase change energy for [7]ivyane and the blend (i.e., heat of fusion) were determined to be 48.6 J/g and 123.1 J/g, respectively, which is close to the average of [7]ivyane and pure paraffin heats of fusion $(0.5(48.6 + 216.1) = 132.3 \text{ J/g})$ as expected for a 1:1 mixture. The DSC results for [6]ivyane using a closed container did not show any sign of a phase transition for the temperature range -50 C to 300 C. That test also showed thermal decomposition occurring at temperatures above 300 C. After the DSC runs the containers were opened and examined, revealing changes in appearance of the ivyane samples.

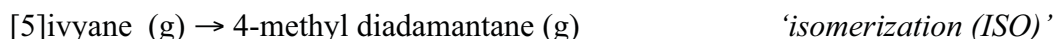
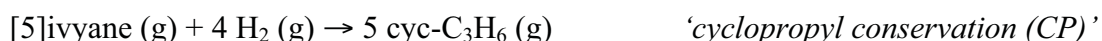
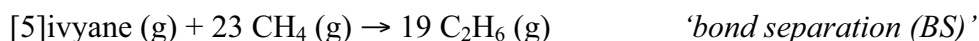
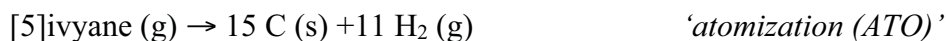
In addition, the density of [6]ivyane was measured using a sample container with a volume of 0.0562 cm^3 . Mass was added to the container until the liquid level was even with the top of the container. The container and sample were then weighed on a scale with precision to 0.0001 g. An average density was calculated based on 4 measurements. The sample masses were 0.0557 g, 0.0547 g, 0.0559 g, and 0.0555 g, which relate to densities of 0.9915 g/cm^3 , 0.9737 g/cm^3 , 0.9950 g/cm^3 , and 0.9879 g/cm^3 . The average density was then 0.9870 g/cm^3 .

3. Modeling of Ivyanes Thermochemical Properties

Modeling of individual gas-phase ivyane molecules is carried out to estimate heats of combustion and formation. We use quantum chemistry methods that involve solving the electronic Schrodinger equation to obtain the ground state electronic energy of a molecule with fixed nuclei. A general description of the approach is given in reference 14. Since the early 1990s, a successively more accurate series of composite methods have been developed with the goal of using quantum chemistry calculations to predict the thermochemical properties of small to medium sized molecules. In these methods, the molecular geometry and harmonic vibration frequencies are first determined at a relatively low level of accuracy and then successive calculations are carried out at that geometry to ascertain the affect of using larger atomic orbital basis set expansions and better treatments of electron correlation. In addition, an empirical correction term is applied to compensate for remaining deficiencies in the method. This empirical correction is constructed to minimize the average error of computed properties such as standard heat of formation, ionization potential and dipole moment for a large test set of small molecules. The first method was called G2¹⁵ and could only be applied to molecules with fewer than 10-15 atoms (including hydrogen). The next method, called G3¹⁶, was further adapted to use a simpler treatment of electron correlation¹⁷ (G3MP2) and finally to utilize density functional theory (DFT) for the initial geometry and harmonic frequency calculation. That composite method is called G3MP2//B3LYP¹⁸ and uses the hybrid DFT functional developed by Becke¹⁹ for balancing the effects of

electron exchange and correlation. Values of standard heats of formation for the 299-molecule test set computed using the G3MP2//B3LYP method have a 5.2 kJ/mol mean absolute deviation with experimental data. This method has been shown to work well for the jet fuel additive JP10 ($C_{10}H_{16}$), which is a strained polycyclic hydrocarbon²⁰. For the current study we use the G3MP2//B3LYP method as implemented in the Gaussian software package²¹.

The enthalpy calculations are straightforward, but in order to obtain standard heats of formation from the total molecular energies one must assume a model chemistry. This is a reaction that relates the energy of a target molecule to other atomic and molecular species with known heats of formation.^{22,23} Several possibilities are illustrated for [5]ivyane ($C_{15}H_{22}$):



The approach is illustrated for the combustion reaction. The heat released by this reaction at $T=298$ K is:

$$\Delta H_{rxn}(298) = 15 H_{CO2(g)} + 11 H_{H2O(l)} - H_{[5]ivyane(g)} - 21.5 H_{O2(g)}$$

(H_x signifies the enthalpy at 298 K for species x). We first compute $\Delta H_{rxn}(298)$ by combining the computed enthalpies of all the reactant and product species determined using the G3MP2//B3LYP method and then equate it with the expression for $\Delta H_{rxn}(298)$ using standard heats of formation for all species (e.g., from the NIST Chemistry Webbook database²⁴) except [5]ivyane, which is treated as the unknown. Previously, the bond separation and isomerization reactions were found to work best for JP10²⁰. The disadvantage with this method is that the errors associated with all the other reactant and product molecules are additive. For larger molecules, these errors in the reference species energies (e.g., CH_4 , C_2H_6 for the bond separation case) are amplified by the large coefficients needed to balance the reaction. A better approach is to use the energy difference between the target molecule and an isomer whose heat of formation is known. Fortunately there are isomers of [3]-[5]ivyane with known heats of formation in the NIST database²⁴. For example, [5]ivyane and 4-methyl diadamantane have the same stoichiometry ($C_{15}H_{22}$). The calculations were carried out for [2]-[6]ivyane, but the larger ivyane molecules are too big for this method to be practical. The results of these calculations are given in Table 1 and in Figures 7 and 8. Note that values are given for gas phase molecules even though these ivyanes are liquids at standard conditions ($T = 298.16$ K and $P = 10^5$ Pa). The dashed lines are extrapolated values for larger ivyane number based on the heat of combustion per unit weight of the ivyane molecule. Also the correction described below for the computed standard heat of combustion has been applied. There is also concern that the empirical correction term added to the computed G3MP2//B3LYP energies might not be accurate for molecules that are much larger than

tany of the ones in the test set. For validation purposes calculations were also carried out for a series of normal alkanes with 4 to 20 carbon atoms. The gas phase and condensed phase standard enthalpies of formation for these molecules are also contained in the NIST database.²⁴ Results for the alkanes are given in Table 2 and Figures 9-11.

Table 1. Gas phase enthalpies of combustion and formation (in kJ/mol) for the ivyane series from G3MP2//B3LYP calculations. Experimental data from NIST (reference 24).

	[1]	[2]	[3]	[4]	[5]	[6]
$\Delta_f H^\circ(g)$ ATO	57.15	138.42	212.09	289.14	360.28	440.41
$\Delta_f H^\circ(g)$ BS	56.84	139.37	214.31	292.63	365.03	446.43
$\Delta_f H^\circ(g)$ CP	53.3	126.21	191.53	260.22	323.00	394.78
$\Delta_f H^\circ(g)$ ISO		138.29	193.33	290.89	374.98	
$\Delta_f H^\circ(g)$ expt	53.3	134.32				
$\Delta_c H^\circ(g)$	-2121.17	-3980.04	-5831.32	-7685.97	-9534.72	-11,392.45
$\Delta_c H^\circ(g)$ corr.	-2095.16	-3928.61	-5754.46	-7583.69	-9407.01	-11,239.32
$\Delta_c H^\circ(g)$ expt	-2091.4	-3886.1				

From Table 1 it is evident that the computed $\Delta_f H^\circ(g)$ based on the bond separation method and atomization reactions are comparable and for [1]- and [2] ivyane (cyclopropane and bicyclopropyl) in excellent agreement with experiment measurements. Use of the cyclopropyl conserving reaction consistently yields lower heats of formation than the other methods, and the differences are increasing with ivyane number. Determination of $\Delta_f H^\circ(g)$ from the isomerization reaction is problematic. In previous work (reference 20) this reaction gave superior results to the bond separation and atomization methods. In that case, the comparison was between JP-10 ($C_{10}H_{16}$) and adamantane – both are polycyclic hydrocarbons with no double bonds. In the present study, the reference molecules for ivyane numbers 2-4 have one or more double bonds and it is possible that the method does not work as well for that case. For [5]ivyane, the reference molecule is 3-methyl diadamantane and one expects the isomerization reaction to yield an accurate value of $\Delta_f H^\circ(g)$. The result for [5]ivyane (374.98 kJ/mol) is 10-15 kJ/mol higher than the results obtained from the bond separation and atomization reactions.

The data in Table 2 $\Delta_f H^\circ(g)$ computed from bond separation and atomization reactions agree extremely well with the experimentally derived values for gas phase alkanes with 4 to 20 carbon atoms (experimental data for larger hydrocarbons is not readily available). However, we observe a large systematic deviation between the computed and experimental²⁴ values for the standard heat of combustion, $\Delta_c H^\circ(g)$ - the difference between experiment and calculation grows from 37.6 kJ/mol for C_4H_{10} to 174.0 kJ/mol for $C_{20}H_{42}$. The source of this discrepancy was traced to errors in the atomization energies for the reference molecules in the combustion reaction, namely O_2 (-3.281 kJ/mol), CO_2 (+4.807 kJ/mol) and H_2O (-1.060 kJ/mol). After adding these

corrections to the G3MP2//B3LYP energies of these species, the recomputed values of $\Delta_c H^\circ(g)$ are all within ± 3 kJ/mol of the experimental values, as seen in Table 2. This correction makes the $\Delta_c H^\circ(g)$ values consistent with the $\Delta_f H^\circ(g)$ computed using the atomization reaction.

Table 2. Gas phase enthalpies of combustion and formation for the normal alkanes from G3MP2//B3LYP calculations. Experimental data from NIST (reference 24). Values in italics are determined by extrapolation. Except as noted, all units are in kJ/mol.

Alkane	$\Delta_f H^\circ$ expt	$\Delta_f H^\circ$ BS	$\Delta_f H^\circ$ ATO	$\Delta_c H^\circ$ expt	$\Delta_c H^\circ$ calc	$\Delta_c H^\circ$ corr.	$\Delta_c H^\circ$ kJ/g
C4H10	-125.6	-125.339	-123.347	-2877.5	-2915.086	-2879.829	-49.652
C5H12	-146.8	-145.967	-143.872	-3535.4	-3582.566	-3538.640	-49.148
C6H14	-167.1	-166.895	-164.696	-4194.9	-4249.747	-4197.152	-48.804
C7H16	-187.8	-187.542	-185.239	-4853.6	-4917.209	-4855.945	-48.559
C8H18	-208.7	-208.520	-206.113	-5511.8	-5584.341	-5514.408	-48.372
C9H20	-228.3	-229.238	-226.727	-6171.6	-6251.732	-6173.130	-48.228
C10H22	-249.7	-250.118	-247.504	-6829.7	-6918.961	-6831.690	-48.110
C11H24	-270.3	-270.978	-268.260	-7487.7	-7586.210	-7490.270	-48.015
C12H26	-290.9	-292.071	-289.250	-8147.5	-8253.226	-8148.617	-47.933
C14H30	-332.1	-333.811	-330.783	-9464.8	-9587.704	-9465.757	-47.807
C16H34	-374.9	-375.289	-372.053	-10,780.5	-10,922.444	-10,783.159	-47.713
C18H38	-414.6	-417.402	-413.959	-12,099.5	-12,256.550	-12,099.927	-47.638
C20H42	-455.8	-459.085	-455.434	-13,417.1	-13,591.085	-13,417.124	-47.578
<i>C22H46</i>			<i>-495.629</i>			<i>-14,735.681</i>	<i>-47.534</i>
<i>C24H50</i>			<i>-534.160</i>			<i>-16,055.830</i>	<i>-47.502</i>
<i>C26H54</i>			<i>-571.921</i>			<i>-17,376.749</i>	<i>-47.477</i>
<i>C28H58</i>			<i>-609.901</i>			<i>-18,697.449</i>	<i>-47.455</i>
<i>C30H62</i>			<i>-647.424</i>			<i>-20,018.606</i>	<i>-47.437</i>
<i>C32H66</i>			<i>-684.605</i>			<i>-21,340.105</i>	<i>-47.422</i>

Table 2 also contains values of the standard heat of combustion in units of kJ/g. This quantity varies much less with alkane size and is a useful quantity for extrapolating thermochemical properties for alkanes with up to $C_{32}H_{66}$, the average molecular composition of paraffin. $\Delta_c H^\circ(g)$ in kg/mol is estimated using the extrapolated kJ/g values and $\Delta_f H^\circ(g)$ is computed from the heat of combustion. These values are also shown in Table 2 and Figure 11. They are then used to derive the extrapolated values of $\Delta_c H^\circ(g)$ (Figure 9) and $\Delta_f H^\circ(g)$ (Figure 10) for the alkanes. Using the same extrapolation method, values of $\Delta_f H^\circ(g)$ and $\Delta_c H^\circ(g)$ are estimated for [7]-[10]ivylene (ivyanes with more than 8 cyclopropyl groups have not yet been synthesized). The extrapolated values are included in Figures 7 and 8. For [6]ivylene $\Delta_f H^\circ(g) = 440.4$ kJ/mol by direct calculation and for [7]- and [8]ivylene $\Delta_f H^\circ(g) = 542.5$ kJ/mol and 647.6 kJ/mol by extrapolation, respectively.

For rocket propulsion applications the relevant heats of formation and combustion for fuel components must be for liquid or solid phase molecules. The calculated values

for normal alkanes and ivyanes are determined for gas phase species. In order to obtain the needed liquid and solid thermochemical data the heat of vaporization or sublimation must be available. For alkane chains up to 20 carbons in length $\Delta_{\text{vap}}H^\circ$ and $\Delta_{\text{sub}}H^\circ$ have been measured. For ivyanes, these quantities are not known. In Figure 12a experimental data for standard heats of vaporization and sublimation of normal alkanes are plotted versus the number of carbon atoms in the molecule. For vaporization, the curve is linear and extrapolation to larger molecules is easily carried out. For sublimation the data are more scattered and only an estimate of the heat of sublimation can be obtained. The extrapolations through $\text{C}_{32}\text{H}_{66}$ are shown in the figure. Our estimate for the standard heat of sublimation for paraffin is estimated to be 250 ± 25 kJ/mol, which when combined with $\Delta_f H^\circ(\text{g}) = -684.6$ kJ/mol, from Table 2, yields a value of -935 ± 25 kJ/mol which is in complete agreement with the value of $\Delta_f H^\circ(\text{s}) = -933$ kJ/mol⁹ cited in the Introduction. From Figure 12b, the estimated value of $\Delta_{\text{vap}}H^\circ$ for [6]ivyane is 75 kJ/mol and for [7]ivyane, the estimated value for $\Delta_{\text{sub}}H^\circ$ is 120 kJ/mol. This makes $\Delta_f H^\circ(\text{l}) = 365$ kJ/mol for [6]ivyane and $\Delta_f H^\circ(\text{s}) = 422$ kJ/mol for [7]ivyane. In reference 9 the results of a calorimetric study of [6]ivyane(l) are presented. That paper has a value of $\Delta_c H^\circ(\text{l}) = -12,300 \pm 600$ kJ/mol which is equivalent to $\Delta_f H^\circ(\text{l}) = +1500 \pm 600$ kJ/mol. In the present study we obtain -11,239 kJ/mol and 365 kJ/mol, respectively, for the same quantities. It was pointed out⁹ that the measured heat of combustion for [6]ivyane(l) is approximately six times the value of $\Delta_c H^\circ(\text{g})$ for cyclopropane. This relationship implies that the strain energy of [6]ivyane is greater than the sum of the cyclopropane strain energies, because [6]ivyane ($\text{C}_{18}\text{H}_{26}$) has 10 fewer hydrogen atoms than six cyclopropane molecules (each one C_3H_6) and five fewer $\text{H}_2\text{O}(\text{l})$ are formed by the combustion reaction. The heat of formation of a single liquid phase water molecule is -285.83 kJ/mol, so the total contribution of these five water molecules to the heat of combustion energy is 1429.15 kJ/mol. Thus, there is a discrepancy in $\Delta_c H^\circ$ for [6]ivyane between the experimental value in reference 9 and the calculations presented in the present paper. However, even though the value we obtain for the standard heat of formation for [6]ivyane is considerably less than the value obtained from the calorimetric measurement⁹, it is still quite high, indicative of the large strain energy in the cyclopropane rings.

We also carried out exploratory calculations to ascertain whether fairly simple chemical modifications of ivyanes could improve its performance as a rocket fuel additive. We selectively added methyl groups to the cyclopropyl rings to determine their effect on the thermochemical properties. Each added methyl group increases the overall H/C ratio slightly without significantly reducing the strain cyclopropyl energy. This approach was tried earlier in the Soviet Union with syntin, which is almost equivalent to [3]ivyane with an added methyl group. We also considered a new result from Sherburn and coworkers²⁵ who have prepared a modification of [3]dendralene with an allenyl group replacing the central C-C double bond. It is expected that the cyclopropanation reaction used to convert dendralenes to ivyanes will result in the formation of a spiropentyl group as shown in figure 13. Spiropentane (C_5H_8) is comprised of two perpendicular cyclopropyl rings with a common vertex, as shown in Figure 14. The central carbon atom is highly strained because it has two pairs of bonds with 60° angles.

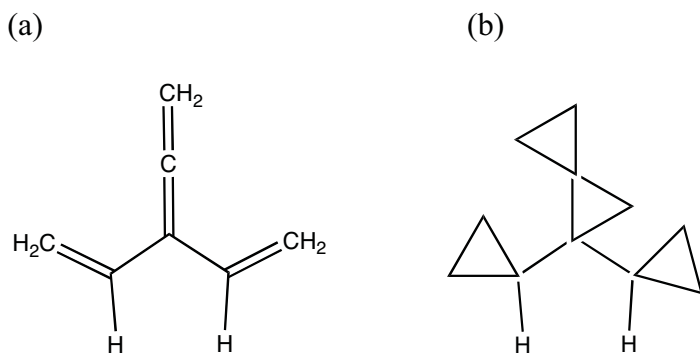


Figure 13. Schematic drawing of (a) 1,1-divinylallene and (b) its cyclopropanation product.

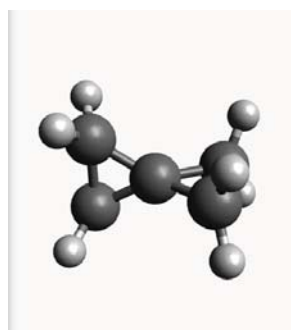


Figure 14. Ball and stick model of spiropentane. The darker spheres represent carbon atoms and the lighter spheres are hydrogen atoms. The carbon-carbon and carbon-hydrogen bonds are indicated.

The results of these calculations are summarized in Table 3. The molecules are arranged with each parent ivyane. It can be seen that converting a cyclopropyl ring to a spiropentyl greatly increases the standard heat of formation. On the other hand, adding methyl groups to the cyclopropyl rings reduces it somewhat. However, the H/C ratio is increased by 0.1 to 0.2 with methylation and reduced by spiropentane formation, so the potential effect on I_{sp} is unclear. Also in that table are heats of formation and combustion for the liquid rocket fuel syntin and cubane, a well-studied HEDM candidate, as well as hypothetical molecules tetrahedrane and ditetrahedryl. Cubane, a solid, and the tetrahedrane molecules, gases at room temperature, have extremely high values of $\Delta_f H^\circ$, but very low H/C ratios. So they are probably not good rocket fuel candidates.

Table 3. Thermochemistry of modified ivyanes and other HEDM candidate fuels as determined by G3MP2//B3LYP calculations

Molecule	$\Delta_f H^\circ$ ATO kJ/mol	$\Delta_f H^\circ$ BS kJ/mol	$\Delta_c H^\circ$ corr. kJ/mol	$\Delta_c H^\circ$ kJ/g	H/C
[2]ivyane	138.42	139.37	-3928.60	-47.9098	1.6667
[2]spiro-ivyane (C ₁₀ H ₁₄)	326.05	329.75	-6261.92	-46.7308	1.4
[3]ivyane	212.09	214.31	-5754.46	-47.1677	1.5556
[3]ivyane, 1-methyl	128.62	130.53	-7708.99	-47.0060	1.6667
[3]ivyane, 1,2-dimethyl	52.89	54.49	-9671.27	-46.9479	1.7333
[3]spiro-ivyane	587.4	593.81	-9348.37	-46.7419	1.3333
[4]ivyane	289.14	292.63	-7583.68	-46.8128	1.5
[4]ivyane, 1-methyl	192.25	195.32	10,204.13	-46.8080	1.625
[5]ivyane	360.28	365.03	-9407.00	-46.5693	1.4667
[5]ivyane, 1-methyl	257.23	261.47	12,700.63	-46.6935	1.6
tetrahydrane (C ₄ H ₄)	538.53	541.27	-2684.21	-51.6195	1
ditetrahydril (C ₈ H ₆)	1093.44	1100.49	-5098.97	-49.9899	0.75
cubane (C ₈ H ₈)	608.37	613.85	-4899.74	-47.1129	1
syntin (C ₁₀ H ₁₆)	186.43	188.55	-6408.13	-47.1186	1.6

4. Evaluation of Ivyanes as Rocket Fuels

In order to predict the performance of new rocket fuels and fuel additives we assume thermochemical equilibrium is achieved at the combustor exit and throughout the nozzle. We use the CEA computer code²⁶⁻²⁸ (Chemical Equilibrium with Applications) that was developed by Gordon and McBride at NASA Glenn Research Center. CEA requires as input the mole fraction, stoichiometry and heat of formation of each fuel and oxidizer component as well as initial fuel temperature, mass of oxidizer to mass of fuel ratio (O/F), pressure at the combustor exit and supersonic area ratio of the nozzle, and computes the exhaust gas temperature at the combustor exit, nozzle throat and exit, and I_{sp} at the nozzle throat and exit. We considered both oxygen (O₂) and nitrous oxide (N₂O) as oxidizers. We determined I_{sp} as a function of O/F for pure paraffin, pure [8]ivyane and a 1:1 blend (by weight) using O₂ and N₂O as oxidizer. All calculations used a combustion chamber pressure of 500 psia and a nozzle area ratio of 300. The results are shown in Figure 15. It can be seen that [8]ivyane has a slightly higher I_{sp} than paraffin and that the

peak I_{sp} is achieved at a lower O/F for both oxidizers. The values of peak I_{sp} are 383.7 at O/F = 2.5 for [8]ivyane versus 380.2 at O/F = 2.75 for paraffin with O_2 and 331.3 at 8.5 and 327.6 at 9.25, respectively, with N_2O . Results for modified [8]ivyanes with O_2 are shown in Figure 16a and similar results with N_2O are shown in Figure 17. At each value of O/F, the differences between ivyanes and paraffin are shown in Figure 16b.

[8]ivyane+200 is approximately equivalent to spiro-ivyane. One can see that the difference in peak I_{sp} between [8]ivyane its methyl derivative is negligible, as the slight lowering of $\Delta_f H^\circ$ is balanced by the slight increase in H/C. On the other hand, spiro-ivyane has a 2 s higher peak I_{sp} than ivyane. These results indicate that ivyanes and methylated ivyanes offer only a small advantage over paraffin as rocket fuel and negligible advantage as a fuel additive. It is possible that spiroivyane-paraffin blends could offer a slight advantage in performance over pure paraffin.

5. Conclusions

We have evaluated the potential benefit of using highly strained hydrocarbons such as the newly synthesized ivyanes as solid rocket fuels or fuel additives using a three pronged approach: experimental characterization of [6]- and [7]ivyane, calculation of their heats of formation and combustion using the G3MP2//B3LYP quantum chemistry method, and estimation of their I_{sp} using a chemical equilibrium model.

We have determined that [7]ivyane forms a stable 1:1 blend, but the melting temperature difference between paraffin and [7]ivyane is too large. [8]ivyane should have a melt temperature closer to that of paraffin. [6]ivyane does not form a good solid blend with paraffin because its melt temperature is well below 0 C, but it could be a good candidate for liquid fuel rocket applications. We could not determine vaporization energy or boiling points of these ivyanes, because they decomposed at temperatures above 200 C.

We have ascertained ivyanes have large positive heats of formation, due to the strain energy inherent in the cyclopropyl moieties. However, the calculated heat of formation for [6]ivyane is considerably less than the experimental value.⁹ The reason for this discrepancy is not known. We have validated our method for computing thermochemical properties with calculations of the heats of formation and combustion of normal alkanes. In addition, we have determined these thermochemical parameters for hypothetical methylated ivyane derivatives and molecules with cyclopropyl groups replaced by spiro-pentyls.

Our predictions of I_{sp} for ivyanes and modified ivyanes show only slight increase of the I_{sp} for paraffin. Thus it does not appear that ivyanes are suitable candidates to replace or augment paraffin as a fuel for hybrid rockets.

Acknowledgement

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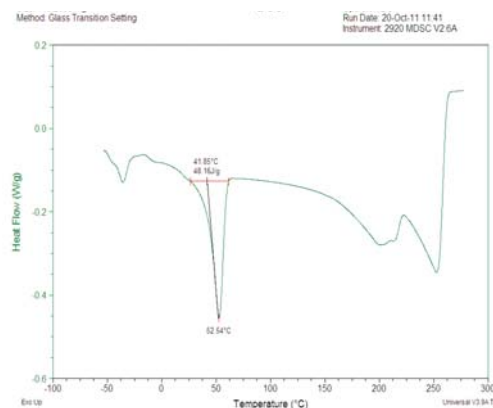
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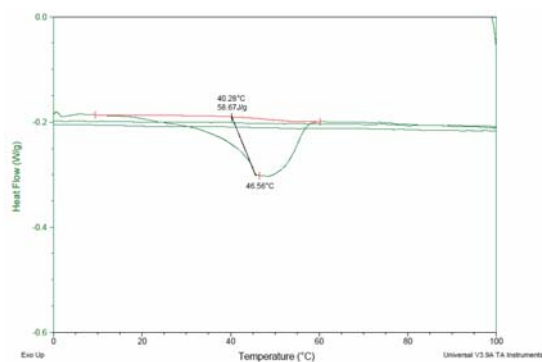
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(a)



(b)



(c)

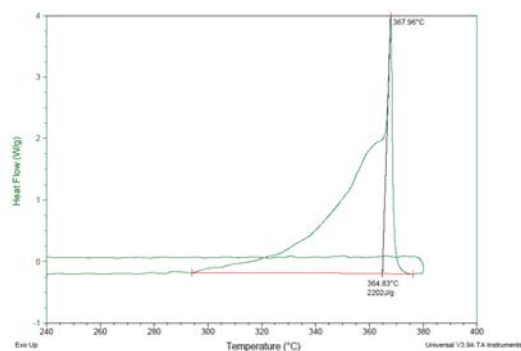


Figure 4. DSC scans for [7]ivylene. (a) result using open sample container with the melt transition at 52.6 C and oxidative decomposition for $T > 200$ C. (b) and (c) result using closed sample container with $T_{mp} = 46.6$ C and non-oxidative decomposition from 300 to 370 C.

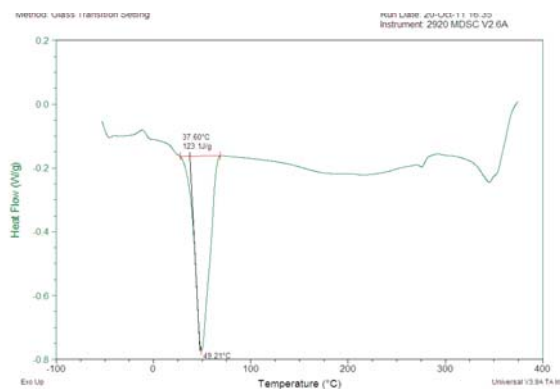


Figure 5. DSC scan for 1:1 paraffin:[7]ivylene blend showing the melt transition at 49.2 C.

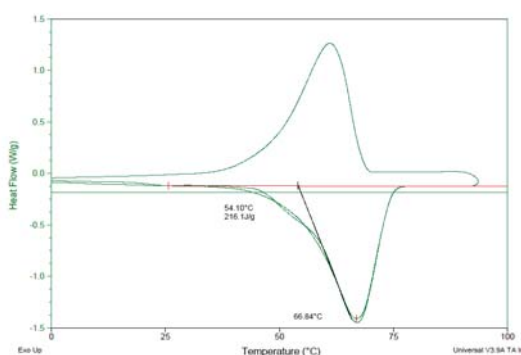


Figure 6. DSC scan for paraffin showing the melt transition at 66.8 C.

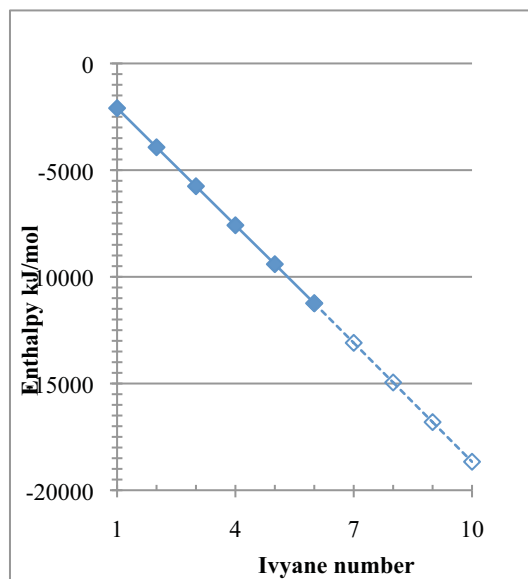


Figure 7. Enthalpy of combustion for gas-phase ivyenes calculated using the G3MP2//B3LYP method. The x-axis is the number of cyclopropane rings and the y-axis is the combustion enthalpy in kJ/mol. Dashed line values derived from extrapolation of $\Delta_c H^\circ$ in kJ/g.

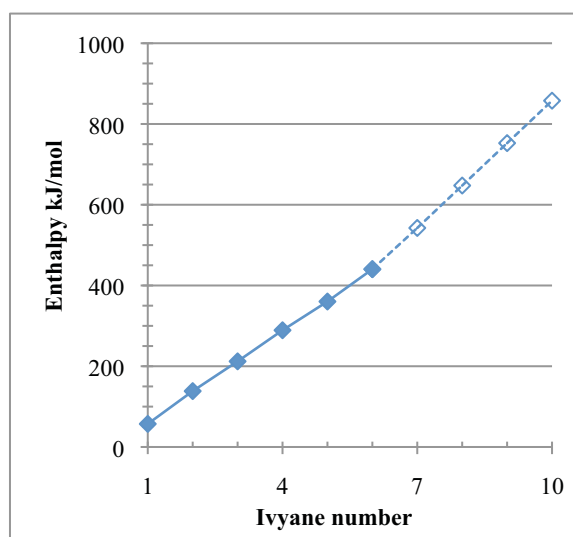


Figure 8. Enthalpy of formation for gas-phase ivyanes calculated using the G3MP2//B3LYP method. The x-axis is the number of cyclopropane rings and the y-axis is the formation enthalpy in kJ/mol. Dashed line values derived from extrapolation of $\Delta_c H^\circ$ in kJ/g.

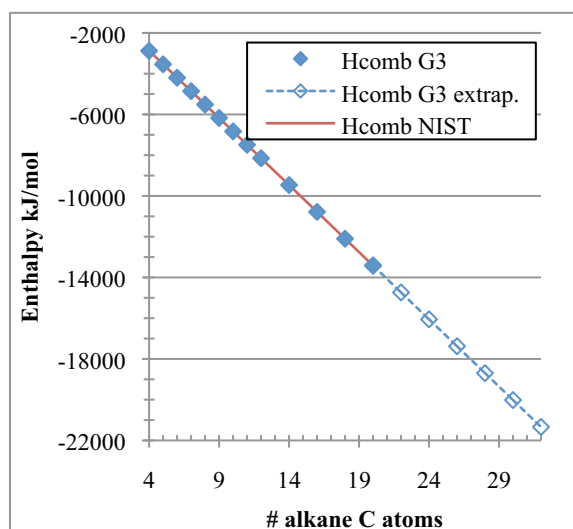


Figure 9. Enthalpy of combustion for gas-phase alkanes calculated using the G3MP2//B3LYP method. The x-axis is the number of carbon atoms in the alkane and the y-axis is the combustion enthalpy in kJ/mol. NIST data are from reference 24.

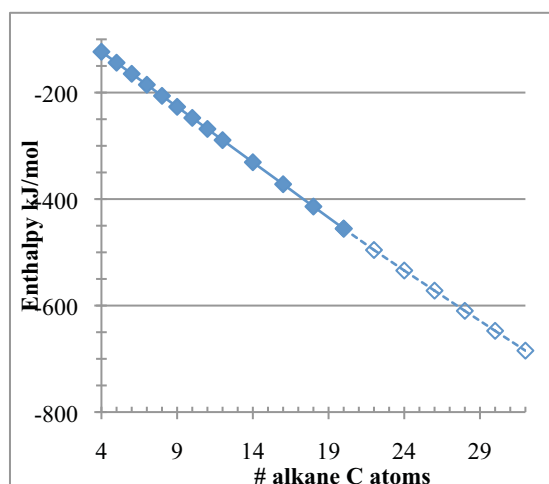


Figure 10. Enthalpy of formation for gas-phase alkanes calculated using the G3MP2//B3LYP method. The x-axis is the number of carbon atoms in the alkane and the y-axis is the combustion enthalpy in kJ/mol. Dashed line values derived from extrapolation of $\Delta_c H^\circ$ in kJ/g.

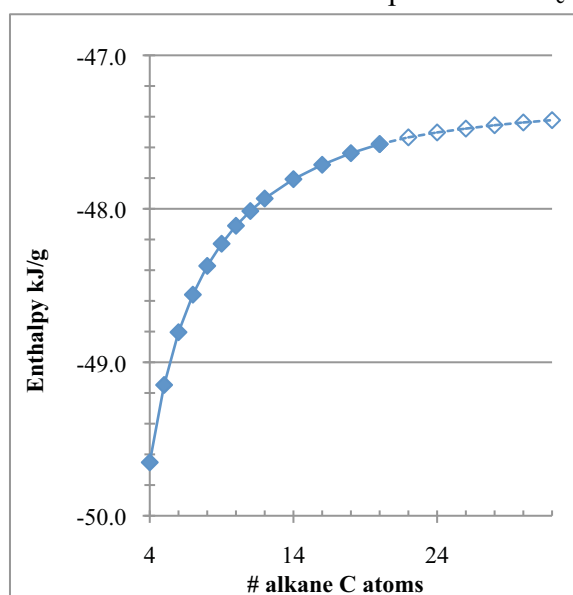
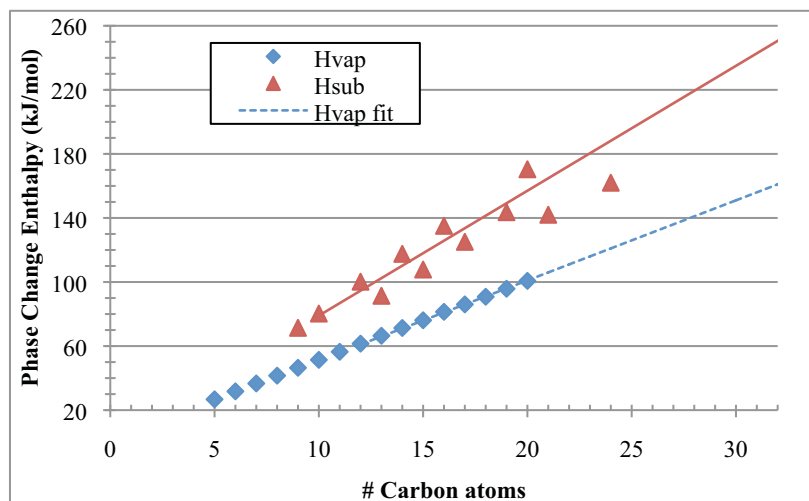


Figure 11. Enthalpy of combustion for gas-phase alkanes calculated using the G3MP2//B3LYP method. The x-axis is the number of carbon atoms in the alkane and the y-axis is the combustion enthalpy in kJ/g. Dash line values are extrapolated as explained in the text.

(a)



(b)

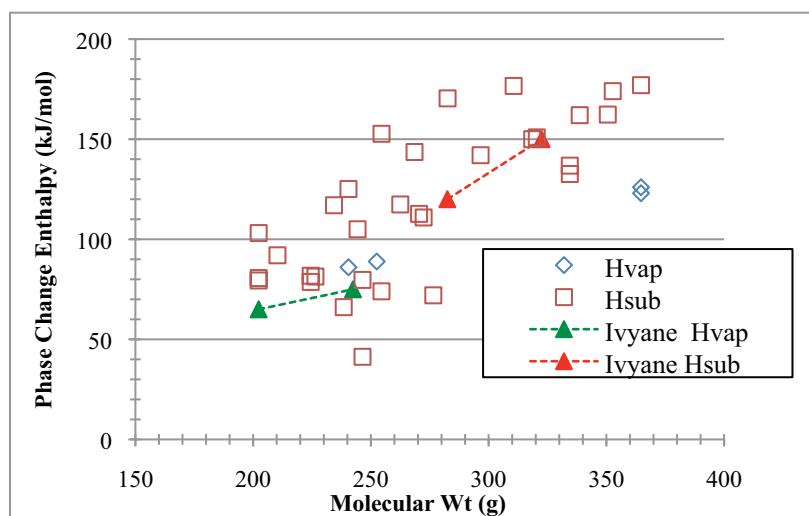


Figure 12. Experimental Phase change enthalpies in kJ/mol for (a) normal alkanes and (b) other alkanes, including estimates for ivyanes from reference 24. Both vaporization and sublimation values are shown.

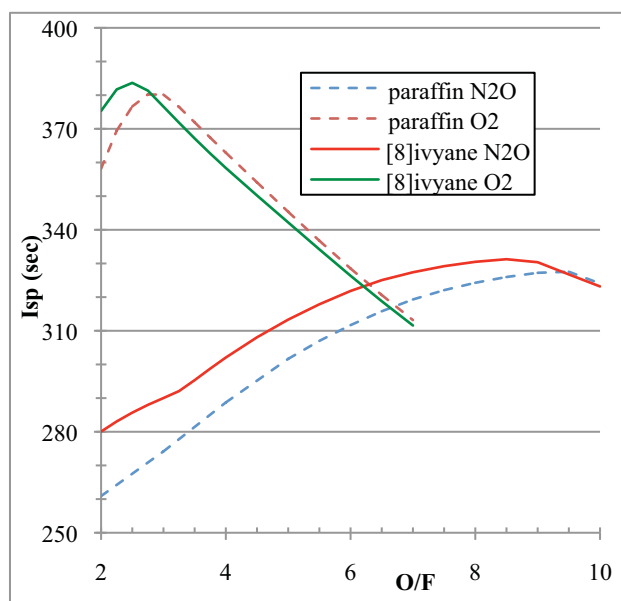


Figure 15. Dependence of I_{sp} on oxidizer to fuel ratio for paraffin and [8]ivyane from CEA calculation for liquid oxygen and N_2O oxidizers.

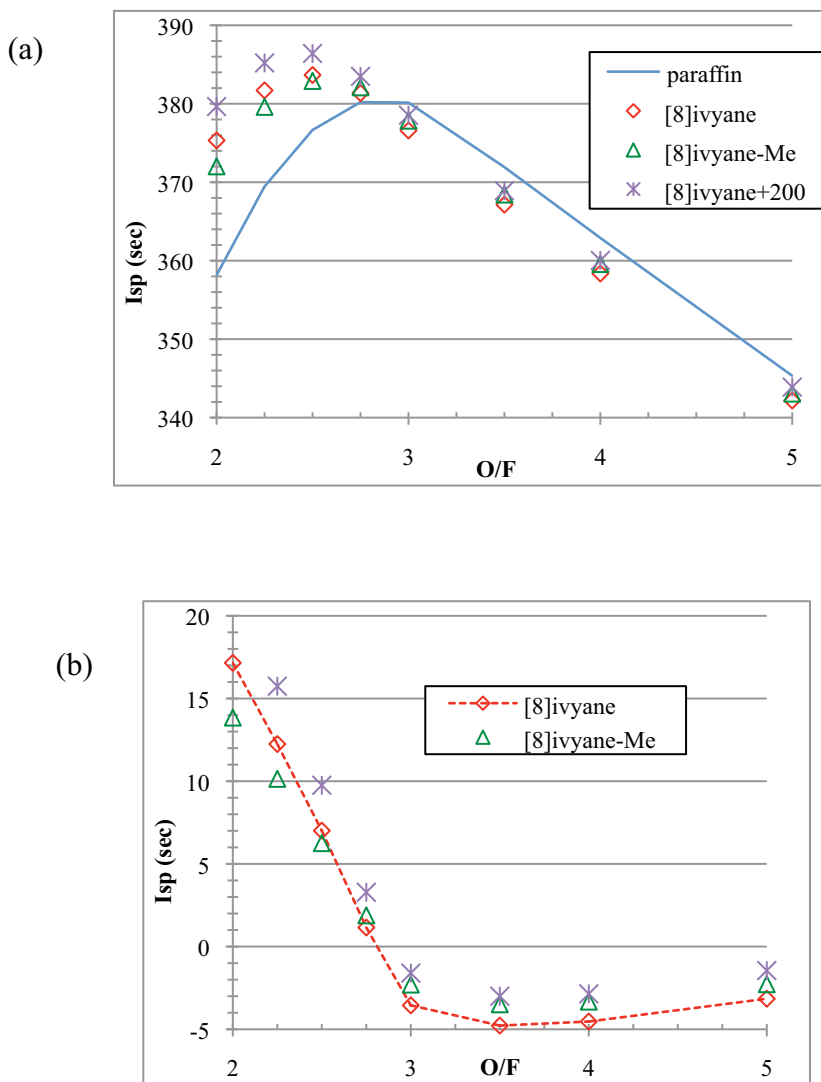


Figure 16. Comparison of I_{sp} for paraffin, [8]ivyane and chemically modified ivyanes using O_2 as oxidizer. (a) I_{sp} and (b) ΔI_{sp} relative to paraffin. [8]ivyane-Me is methylated ivyane and [8]ivyane+200 is ivyane with $\Delta_f H^\circ$ increased by 200 kJ/mol to mimic spiro-ivyane.

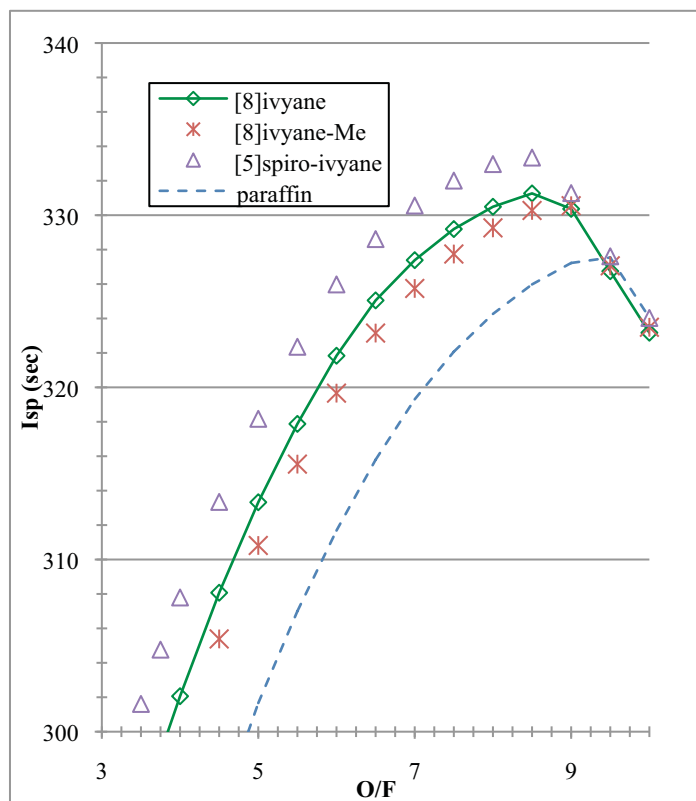


Figure 17. Comparison of I_{sp} for paraffin, [8]ivyane and chemically modified ivyanes using N_2O as oxidizer.